

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C07C 253/26		A1	(11) International Publication Number: WO 96/25391 (43) International Publication Date: 22 August 1996 (22.08.96)
(21) International Application Number: PCT/US96/02206		(74) Agent: PASSLEY, Paul, Leonard; Monsanto Company, 800 North Lindbergh Boulevard, St.Louis, MO 63167 (US).	
(22) International Filing Date: 16 February 1996 (16.02.96)			
(30) Priority Data: 08/390,726 17 February 1995 (17.02.95) US		(81) Designated States: AL, AM, AU, AZ, BB, BG, BR, BY, CA, CN, CZ, EE, FI, GE, HU, IS, JP, KG, KR, KZ, LK, LR, LT, LV, MD, MG, MK, MN, MX, NO, NZ, PL, RO, RU, SG, SI, SK, TJ, TM, TR, TT, UA, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).	
(60) Parent Application or Grant (63) Related by Continuation US Filed on 08/390,726 (CIP) 17 February 1995 (17.02.95)		Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(71) Applicant (<i>for all designated States except US</i>): MONSANTO COMPANY [US/US]; 800 North Lindbergh Boulevard, St. Louis, MO 63167 (US).			
(72) Inventors; and (75) Inventors/Applicants (<i>for US only</i>): BRAUN, John, Ferrell [US/US]; 746 Seacliff, Houston, TX 77062 (US). NOWAK, Robert, Thomas [US/US]; 1709 Falcon Ridge Boulevard, Friendswood, TX 77546 (US). ROOKS, Charles, Wendell [US/US]; 15330 Torry Pines, Houston, TX 77062 (US). STEINMEYER, Daniel, Eric [US/US]; 2008 Wilson Ridge Lane, Chesterfield, MO 63005 (US).			

(54) Title: REDUCTION OF AMMONIA WASTES ASSOCIATED WITH AMMOXIDATION PROCESSES

(57) Abstract

Ammonia effluent from fluid bed processes for catalytic ammonoxidation of propylene to form acrylonitrile are reduced by introduction of methanol into the fluid bed at selected locations.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russia Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LJ	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MIR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

- 1 -

REDUCTION OF AMMONIA WASTES
ASSOCIATED WITH AMMOXIDATION PROCESSES

BACKGROUND OF THE INVENTION

This application is a continuation-in-part of
5 United States patent application serial number
08/390,726 filed February 17, 1995 and copending
herewith.

The invention relates to reduction of ammonia
wastes produced in processes for production of
10 acrylonitrile by catalytic ammoxidation of propylene in
a fluidized bed reaction.

Commercial processes for production of
acrylonitrile by passage of propylene, oxygen (air),
and ammonia through a fluidized bed of ammoxidation
15 catalyst are well known by those skilled in the art.
In such processes an excess of ammonia is commonly
employed and necessary to obtain high levels of
conversion of propylene to acrylonitrile. As a result,
significant levels of ammonia are present in the
20 product stream and must be recovered and/or converted
to other waste products such as ammonium nitrates or
sulfates at considerable expense.

The addition of methanol to processes of
catalytic ammoxidation of propylene to acrylonitrile in
25 order to increase hydrogen cyanide co-product
production and, to some extent, consume excess ammonia
is known. It is further known that methanol can
compete with propylene in ammoxidation reactions and
difficulty may be experienced in preventing reduction
30 in acrylonitrile yields.

It will be appreciated by those skilled in
the art that processes for reducing ammonia wastes
without seriously impairing conversion of propylene to
35 acrylonitrile are desired from the standpoint of both
economic and environmental considerations.

- 2 -

SUMMARY OF THE INVENTION

The invention is based on the discovery that in a process for making acrylonitrile by passing propylene, oxygen (air), and ammonia through a 5 fluidized bed of ammonoxidation catalyst, the amount of ammonia contained in the product stream can be effectively and economically reduced without substantial adverse effect on acrylonitrile yield by introducing methanol into the reactor under non-coking 10 conditions at a point and in an amount such that ammonia in the reactor effluent is substantially reduced without undue reduction in acrylonitrile yield. This continuation is particularly directed to the prevention of blockage of the methanol addition means 15 used in the process. The invention will be fully understood from the following description of the preferred embodiments.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In accordance with this invention, methanol 20 is introduced into a fluidized bed reaction system in which a bed of ammonoxidation catalyst is fluidized by a flow of the reactants, propylene, ammonia, and oxygen containing gas (air). The use of such systems for the manufacture of acrylonitrile is well known.

Essentially any of the numerous catalysts 25 known for the ammonoxidation of propylene can be employed using conventional ammonoxidation reaction conditions. For example, catalysts mainly consisting of bismuth phosphates or molybdates or of antimony and uranium 30 oxides or of bismuth phosphates or molybdates doped with iron, nickel, cobalt etc., or of antimony oxide and oxides of metals such as iron, cobalt, or nickel may be used. A particularly preferred catalyst is represented by the formula $Sb_aU_bFe_cBi_dMo_eMe_fO_g$, in which Me 35 is nickel or cobalt, a is 1 to 10, b is 0.1 to 5, c is 0.1 to 5, d is 0.001 to 0.1, e is 0.001 to .1, f is 0

- 3 -

to 0.1 and g is a number taken to satisfy the valences of the quantities of other components present.

Ammonoxidation processes using catalysts of this type are described, for example, in U.S. Patents 4,018,712,

5 4,545,943, and 4,487,850, the disclosures of these patents being incorporated herein by reference.

The methanol will be introduced at a point and in an amount such that the ammonia content of the reactor effluent will be less than 0.5 mole percent and
10 lower than if no methanol were introduced and such that acrylonitrile production measured as weight per unit of time is at least 97% by weight of what would be obtained if no methanol were introduced. Preferably, ammonia effluent will be less than 0.25 mole percent
15 or, most preferably, substantially eliminated with less than 1% reduction in acrylonitrile production.

In a preferred embodiment of the invention, the methanol is introduced into the fluidized bed reactor at a point where 5% to 60% by weight of the catalyst in the reactor is above the methanol introduction point. Such point can be determined by calculational methods well understood by those skilled in the fluid bed art or by actual measurement techniques based, for example, on pressure measurements made at various reactor heights. The weight of the catalyst above the injection point refers to the weight when the bed is fluidized under operating conditions. Also, it is contemplated that the catalyst charge will be an amount chosen to ensure complete ammonoxidation of
25 the propylene but without undue excess. The optimum point of introduction may vary depending on how much excess catalyst, if any, is present; catalyst activity; surface area; etc. For any system, the optimum injection point can be determined by routine testing
30 conducted in light of the disclosure herein.

The amount of methanol used will be sufficient to react with a major portion of the ammonia

- 4 -

not reacted with propylene. However it is desirable to avoid excesses of methanol which would be expensive to separate from the acrylonitrile product. Preferably, the methanol content of the effluent will be less than 5 0.25 mole percent, most preferably, less than 0.01 mole percent. Generally, the use of from 0.8 to 2.0 times the moles stoichiometrically required to react with the ammonia in excess of that required for the ammonoxidation of propylene will give satisfactory results.

10 Like the optimum point of methanol introduction, the amount of methanol to be utilized will depend upon the catalyst in use and the amount present; the quantities of other reactants present; and flow rates in the fluidized bed system. It is 15 preferred to introduce the methanol in a downward direction so that the openings through which it is introduced will not become clogged when the reactor is shut down or methanol flow is stopped for maintenance or other reasons.

20 Since the methanol introduction means will generally be of relatively small dimensions and, more importantly, may not be operated continuously, care should be taken to prevent blockage. It is particularly preferred, in order to prevent clogging or 25 blockage in the sparger, tube, or other means through which methanol is introduced, that a gas flow in addition to methanol be maintained at all times that a catalyst charge is present on the reactor, even if the reactor bed is not fluidized. The gas can be any inert 30 gas which is defined as a gas which will not adversely affect the reaction or reactor materials of construction. For example, nitrogen or carbon dioxide can generally be used at any time. Air can be used in amounts which will not form explosive mixtures with 35 methanol (or in any amount if the reactor is "down" or if methanol is not being introduced into the reaction). Steam can be conveniently and advantageously used if

- 5 -

the reaction is in progress. Mixtures of gases can be used. The gas flow linear velocity through the orifices of the methanol introduction means should exceed (preferably by ten to fifty times) the linear 5 velocity of other gases through the fluid bed reactor. If the reactor is "down" and no gas flow, for example, from purges of the reactant inlets, is present, it is still desirable to maintain a minimal flow to ensure catalyst fines are not drawn into the methanol 10 introduction means. It is further desirable that the openings in the sparger, tube, or other means through which methanol is introduced be significantly larger than the catalyst particles present in the reactor. More specifically, the diameters of the openings (or 15 smallest dimension of the opening if non-round openings are used) should be at least ten, preferably, at least twenty or thirty times the mean particle size of the largest 10% by weight of the catalyst particles. There is no upper limit on opening size except such as may be 20 dictated by considerations of gas flow patterns and rates which may also render it desirable to decrease the number of openings as opening size increases.

It is known that methanol in contact with iron or iron containing alloys or materials of 25 construction will undergo reactions leading to coking at elevated temperatures such as commonly employed in ammonoxidation reactions. In order to minimize down time for cleaning coked reactor inlet lines and spargers, it is important that the methanol be introduced under non- 30 coking conditions. This can be accomplished by use of non-ferrous or high molybdate containing stainless steel inlet lines and spargers, but the expense may be undesirable. Alternatively, the portion of the inlet line between the reactor inlet point and point of 35 discharge can be insulated to maintain the temperature of the conduit below coking temperature but this is frequently inconvenient and the space occupied inside

- 6 -

the reactor by an insulated conduit may interfere with fluid bed flow patterns. In accordance with the present invention, it is preferred to prevent major coking by vaporizing the methanol prior to the point
5 the methanol inlet line enters the reactor and by locating the inlet line entry point as close to its point of discharge (the sparger) inside the reactor as possible.

In order to prevent coking, it is
10 particularly preferred to mix the methanol with water vapor (steam) and/or air. Steam is preferred in order to prevent the possible formation of combustible or explosive mixtures. Coking can generally be adequately prevented by the use of a mixture of methanol with at
15 least 20 mole percent steam or air or mixture thereof. The use of additional steam or air (or other gas which does not adversely affect the reaction system) may be desirable to provide a volume of gas flow sufficient to assure good distribution of the methanol in the fluid
20 bed system. However, the amount of air, if any, mixed with the methanol should not be so great as to form a flammable mixture.

Minor modifications in the primary acrylonitrile process may be desirable to optimize
25 production of acrylonitrile and, if desired, co-products such as hydrogen cyanide. Better hydrogen cyanide yields and less loss of acrylonitrile are experienced if the oxygen (air) to propylene ratio is increased so that the oxygen exiting the reaction is
30 about the same as in the case of the conventional (no methanol present) process for ammoxidation of propylene. The oxygen (air) should be sufficient to prevent catalyst reduction but not so great as to form explosive mixtures.

35 The practice of the invention and its comparison with conventional processes is further illustrated by the following examples.

- 7 -

EXAMPLES I-XVII

In these examples, a 4.1 cm inside diameter by 1.8 meter high fluidized bed reactor constructed of 316 stainless steel is used. The outlet end of the
5 reactor is connected to a gas chromatograph for analysis of effluent gases. Propylene, ammonia and air feeds are supplied via mass flow controllers and are premixed before being brought into contact with the fluidized bed. The methanol is fed separately by a
10 positive displacement pump and is vaporized by heating prior to being introduced into the reactor. The reactor contains the amount shown in Table 1 below of catalyst indicated. Catalyst number 1 has the following composition:



(O_x indicates the elements are present as their oxides and the composition contains sufficient oxygen to satisfy their valences) which is deposited on 50% by weight SiO_2 carrier. Catalyst 2 is a mixture of iron
20 and antimony oxides deposited on a silica carrier. Catalyst 3 is a mixture of bismuth, molybdenum, and iron oxides on a silica carrier.

Since catalyst activity may vary somewhat with extended usage, each example compares a limited
25 number of successive runs with methanol in the feed stream against a control in which no methanol is introduced.

In all cases, an inert gas flow through the methanol sparger openings (which are about thirty times
30 the diameter of the mean particle size of the largest 10% by weight of the catalyst particles) at a linear velocity about 30 times greater than the linear velocity of the flow of other gases through the reactor is maintained. No clogging of the sparger is observed.

35 No coking is observed in the examples.

- 8 -

TABLE 1

	Example I		Example II	
CATALYST:	1	1	1	1
REACTOR CONDITIONS :				
REACTOR TEMP	deg C	458	458	459
REACTOR PRESS	atms	2.02	2.02	2.01
METHANOL INJ POINT	cm's	41.91	41.91	41.91
WT % of CATALYST ABOVE the MeOH INJECTION PT.	%		3.91	3.91
CATALYST CHARGE	gms	340	340	340
REACTOR FEEDS :				
NH3 FEED	MOL/HR	1.427	1.427	1.419
C3H6 FEED	MOL/HR	1.299	1.299	1.299
AIR FEED	MOL/HR	14.25	14.249	14.243
N2 FEED (w/MeOH)	MOL/HR	0.387	0.387	0.387
METHANOL FEED	MOL/HR		0.193	0.152
NH3/C3H6 FEED	RATIO	1.098	1.098	1.092
AIR/C3H6 FEED	RATIO	10.967	10.966	10.961
MeOH/C3H6 FEED	RATIO		0.148	0.117
EFFLUENT CONDITIONS :				
MOLE % NH3 in EFFLUENT		0.558	0.156	0.450
MOLE % O2 in EFFLUENT		3.056	2.640	3.334
MOLES METHANOL OUT			0.085	0.091
MOLES MeOH FEED / MOLE NH3 IN BC EFFLUENT			1.90	1.85
PROPYLENE CONVERSION	mole %	98.751	98.207	98.487
METHANOL CONVERSION	mole %		56.171	40.253
PRODUCT RESULTS and RESULTS :				
AN MAKE	gms/hr	56.378	56.810	56.444
HCN MAKE	gms/hr	6.891	7.198	6.481
RATIO HCN /AN	gms HCN/gm AN	0.122	0.127	0.114
NH3 Breakthrough	gms/hr	1.729	0.492	1.393
NH3 Reduction	gms/hr		1.237	0.532

- 9 -

TABLE 1

	Example III		Example IV	
CATALYST:	1	1	1	1
REACTOR CONDITIONS :				
REACTOR TEMP	deg C	459	459	457
REACTOR PRESS	atms	2.02	2.02	2.02
METHANOL INJ POINT	cans	41.91	41.91	33.02
WT % of CATALYST ABOVE the MeOH INJECTION PT.	%		3.91	24.29
CATALYST CHARGE	gms	340	340	340
REACTOR FEEDS :				
NH3 FEED	MOL/HR	1.418	1.418	1.423
C3H6 FEED	MOL/HR	1.299	1.299	1.304
AIR FEED	MOL/HR	14.242	14.243	14.24
N2 FEED (w/MeOH)	MOL/HR	0.387	0.387	0.387
METHANOL FEED	MOL/HR		0.152	0.169
NH3/C3H6 FEED	RATIO	1.091	1.091	1.091
AIR/C3H6 FEED	RATIO	10.961	10.961	10.917
MeOH/C3H6 FEED	RATIO		0.117	0.130
EFFLUENT CONDITIONS :				
MOLE % NH3 in EFFLUENT		0.422	0.143	0.474
MOLE % O2 in EFFLUENT		3.308	2.968	3.132
MOLES METHANOL OUT			0.040	0.017
MOLES MeOH FEED / MOLE NH3 IN BC EFFLUENT			1.98	1.96
PROPYLENE CONVERSION	mole %	98.265	97.452	98.284
METHANOL CONVERSION	mole %		73.824	89.740
PRODUCT RESULTS and RESULTS :				
AN MAKE	gms/hr	57.442	57.316	55.694
HCN MAKE	gms/hr	6.472	7.887	6.831
RATIO HCN /AN	gms HCN/gm AN	0.113	0.138	0.123
NH3 Breakthrough	gms/hr	1.306	0.449	1.469
NH3 Reduction	gms/hr		0.857	0.353
				1.116

- 10 -

TABLE 1

Example V

CATALYST:

1	1
---	---

REACTOR CONDITIONS :

REACTOR TEMP	deg C	457	458
REACTOR PRESS	atmos	2.02	2.01
METHANOL INJ POINT	cm's	33.02	33.02
WT % of CATALYST ABOVE the MeOH INJECTION PT.	%	24.29	
CATALYST CHARGE	gms	340	340

REACTOR FEEDS :

NH3 FEED	MOL/HR	1.422	1.422
C3H6 FEED	MOL/HR	1.304	1.304
AIR FEED	MOL/HR	14.238	14.24
N2 FEED (w/MeOH)	MOL/HR	0.387	0.387
METHANOL FEED	MOL/HR		0.169
NH3/C3H6 FEED	RATIO	1.080	1.080
AIR/C3H6 FEED	RATIO	10.016	10.017
MeOH/C3H6 FEED	RATIO		0.130

EFFLUENT CONDITIONS :

MOLE % NH3 in EFFLUENT	0.488	0.119
MOLE % O2 in EFFLUENT	2.926	2.247
MOLES METHANOL OUT		0.009
MOLES MeOH FEED / MOLE NH3 IN BC EFFLUENT		1.91
PROPYLENE CONVERSION	mole %	98.484
METHANOL CONVERSION	mole %	97.596
		94.886

PRODUCT RESULTS and RESULTS :

AN MAKE	gms/hr	55.280	54.459
HCN MAKE	gms/hr	6.961	8.703
RATIO HCN /AN	gms HCN/gm AN	0.126	0.160
NH3 Breakthrough	gms/hr	1.513	0.375
NH3 Reduction	gms/hr		1.138

- 11 -

TABLE 1

Example VI

CATALYST:

1	1	1	1	1
---	---	---	---	---

REACTOR CONDITIONS :

REACTOR TEMP deg C
 REACTOR PRESS atm
 METHANOL INJ POINT cmc
 WT % of CATALYST ABOVE
 the MeOH INJECTION PT. %
 CATALYST CHARGE gms

457	457	457	457	456
2.02	2.02	2.02	2.02	2.02
41.91	41.91	41.91	41.91	41.91
	25.75	25.75	25.75	25.75
440	440	440	440	440

REACTOR FEEDS :

NH3 FEED MOL/HR
 C3H6 FEED MOL/HR
 AIR FEED MOL/HR
 N2 FEED (w/MeOH) MOL/HR
 METHANOL FEED MOL/HR
 NH3/C3H6 FEED RATIO
 AIR/C3H6 FEED RATIO
 MeOH/C3H6 FEED RATIO

1.427	1.428	1.427	1.427	1.427
1.299	1.300	1.300	1.300	1.300
14.248	14.249	14.248	14.248	14.248
0.387	0.387	0.387	0.387	0.387
0.199	0.199	0.199	0.199	0.199
1.098	1.098	1.097	1.097	1.097
10.965	10.958	10.957	10.957	10.955
0.153	0.115	0.071	0.071	0.192

EFFLUENT CONDITIONS :

MOLE % NH3 in EFFLUENT
 MOLE % O2 in EFFLUENT
 MOLES METHANOL OUT
 MOLES MeOH FEED /MOLE NH3 IN BC EFFLUENT
 PROPYLENE CONVERSION mole %
 METHANOL CONVERSION mole %

0.558	0.128	0.133	0.250	0.020
2.185	1.403	1.556	1.731	1.120
	0.002	0.001	0.001	0.003
	1.95	1.47	0.91	2.45
100.000	99.716	99.607	99.795	99.427
	99.229	99.237	99.292	98.814

PRODUCT RESULTS and RESULTS :

AN MAKE gms/hr
 HCN MAKE gms/hr
 RATIO HCN /AN gms HCN/gm AN
 NH3 Breakthrough gms/hr
 NH3 Reduction gms/hr

55.312	55.996	54.722	55.274	50.092
7.229	8.930	8.859	8.503	8.840
0.131	0.159	0.162	0.154	0.176
1.734	0.406	0.419	0.784	0.064
	1.328	1.315	0.950	1.670

- 12 -

TABLE 1

Example VII

CATALYST:

1	1	1
---	---	---

REACTOR CONDITIONS :

REACTOR TEMP	deg C	461	461	461
REACTOR PRESS	atms	2.02	2.02	2.02
METHANOL INJ POINT	cmes	41.91	41.91	41.91
WT % of CATALYST ABOVE the MeOH INJECTION PT.	%		14.03	14.03
CATALYST CHARGE	gms	380	380	380

REACTOR FEEDS :

NH3 FEED	MOL/HR	1.425	1.425	1.425
C3H6 FEED	MOL/HR	1.299	1.299	1.299
AIR FEED	MOL/HR	14.258	14.257	14.259
N2 FEED (w/MeOH)	MOL/HR	0.374	0.374	0.374
METHANOL FEED	MOL/HR		0.159	0.319
NH3/C3H6 FEED	RATIO		1.097	1.097
AIR/C3H6 FEED	RATIO		10.977	10.976
MeOH/C3H6 FEED	RATIO		0.122	0.245

EFFLUENT CONDITIONS :

MOLE % NH3 in EFFLUENT		0.819	0.310	0.037
MOLE % O2 in EFFLUENT		3.845	2.933	2.317
MOLES METHANOL OUT			0.012	0.042
MOLES MeOH FEED /MOLE NH3 IN BC EFFLUENT				1.07
PROPYLENE CONVERSION	mole %	98.705	98.249	97.855
METHANOL CONVERSION	mole %		92.411	88.732

PRODUCT RESULTS and RESULTS :

AN MAKE	gms/hr	54.790	53.652	53.895
HCN MAKE	gms/hr	7.307	10.126	10.936
RATIO HCN /AN	gms HCN/gms AN	0.133	0.189	0.203
NH3 Breakthrough	gms/hr	2.541	0.977	0.118
NH3 Reduction	gms/hr		1.564	2.423

TABLE 1

CATALYST:	Example VIII			Example IX		
	1	1	1	1	1	1
REACTOR CONDITIONS :						
REACTOR TEMP deg C	461	462	461	461	460	460
REACTOR PRESS atms	2.02	2.02	2.02	2.02	2.02	2.02
METHANOL INJ POINT cm's	41.91	41.91	41.91	41.91	41.91	41.91
WT % of CATALYST ABOVE the MeOH INJECTION PT. %		14.03	14.03		18.33	
CATALYST CHARGE gms	380	380	380	400	400	400
REACTOR FEEDS :						
NH3 FEED MOL/HR	1.425	1.425	1.425	1.428	1.428	1.428
C3H6 FEED MOL/HR	1.299	1.299	1.299	1.299	1.299	1.299
AIR FEED MOL/HR	14.258	14.257	14.506	14.266	14.269	14.269
N2 FEED (w/MeOH) MOL/HR	0.374	0.374	0.374	0.374	0.374	0.374
METHANOL FEED MOL/HR		0.317	0.317		0.222	
NH3/C3H6 FEED RATIO	1.097	1.097	1.097	1.099	1.099	1.099
AIR/C3H6 FEED RATIO	10.977	10.976	11.168	10.983	10.986	10.986
MeOH/C3H6 FEED RATIO		0.244	0.244		0.171	
EFFLUENT CONDITIONS :						
MOLE % NH3 in EFFLUENT	0.798	0.000	0.000	0.808	0.120	
MOLE % O2 in EFFLUENT	3.442	2.047	2.514	2.904	2.042	
MOLES METHANOL OUT		0.102	0.101		0.014	
MOLES MeOH FEED / MOLE NH3 IN BC EFFLUENT		2.18	2.18		2.00	
PROPYLENE CONVERSION mole %	99.027	98.128	97.790	99.068	98.522	
METHANOL CONVERSION mole %		67.946	68.104		93.548	
PRODUCT RESULTS and RESULTS :						
AN MAKE gms/hr	54.496	54.158	54.079	54.783	54.156	
HCN MAKE gms/hr	7.518	10.070	10.146	7.518	9.659	
RATIO HCN /AN gms HCN/gm AN	0.138	0.186	0.188	0.137	0.182	
NH3 Breakthrough gms/hr	2.477	0.000	0.000	1.889	0.381	
NH3 Reduction gms/hr		2.477	2.477		1.506	

- 14 -

TABLE 1

	Example X			Example XI		
CATALYST:	1	1	1	1	1	1
REACTOR CONDITIONS :						
REACTOR TEMP	deg C	460	461	461	460	461
REACTOR PRESS	atm	2.02	2.02	2.02	2.02	2.02
METHANOL INJ POINT	cm's	41.91	41.91	41.91	41.91	41.91
WT % of CATALYST ABOVE the MeOH INJECTION PT.	%	18.33	18.33	18.33	18.33	18.33
CATALYST CHARGE	gms	400	400	400	400	400
REACTOR FEEDS :						
NH3 FEED	MOL/HR	1.428	1.427	1.428	1.427	1.427
C3H6 FEED	MOL/HR	1.299	1.299	1.299	1.299	1.300
AIR FEED	MOL/HR	14.285	14.281	14.318	14.526	14.537
N2 FEED (w/MeOH)	MOL/HR	0.374	0.374	0.374	0.374	0.374
METHANOL FEED	MOL/HR	0.278	0.333	0.333	0.333	0.333
NH3/C3H6 FEED	RATIO	1.089	1.089	1.089	1.099	1.098
AIR/C3H6 FEED	RATIO	10.983	10.980	11.023	11.184	11.183
MeOH/C3H6 FEED	RATIO		0.214	0.257		0.256
EFFLUENT CONDITIONS :						
MOLE % NH3 in EFFLUENT		0.544	0.020	0.020	0.559	0.017
MOLE % O2 in EFFLUENT		2.850	1.761	1.431	2.954	1.594
MOLES METHANOL OUT			0.034	0.000		0.034
MOLES MeOH FEED / MOLE NH3 IN BC EFFLUENT			2.80	3.36		3.22
PROPYLENE CONVERSION	mole %	99.349	98.457	98.034	99.475	98.271
METHANOL CONVERSION	mole %		87.514	100.000		89.923
PRODUCT RESULTS and RESULTS :						
AN MAKE	gms/hr	55.335	55.782	54.818	54.808	54.545
HCN MAKE	gms/hr	7.414	9.648	10.948	7.512	10.129
RATIO HCN /AN	gms HCN/gms AN	0.134	0.173	0.200	0.137	0.186
NH3 Breakthrough	gms/hr	1.690	0.064	0.064	1.762	0.055
NH3 Reduction	gms/hr		1.626	1.626		1.707

TABLE 1

	Example XII		Example XIII		
CATALYST:	2	2	3	3	3
REACTOR CONDITIONS :					
REACTOR TEMP	deg C	451	449	460	459
REACTOR PRESS	atms	2.02	2.02	2.02	2.02
METHANOL INJ POINT	cm's	41.91	41.91	41.91	41.91
WT % of CATALYST ABOVE the MeOH INJECTION PT.	%		43.88		26.52
CATALYST CHARGE	gms	650	650	578	578
REACTOR FEEDS :					
NH3 FEED	MOL/HR	1.359	1.360	1.562	1.562
C3H6 FEED	MOL/HR	1.299	1.299	1.299	1.299
AIR FEED	MOL/HR	15.659	15.658	13.312	13.311
N2 FEED (w/MeOH)	MOL/HR	0.374	0.374	0.374	0.374
METHANOL FEED	MOL/HR		0.278		0.139
NH3/C3H6 FEED	RATIO	1.046	1.047	1.203	1.203
AIR/C3H6 FEED	RATIO	12.056	12.055	10.249	10.248
MeOH/C3H6 FEED	RATIO		0.214		0.107
EFFLUENT CONDITIONS :					
MOLE % NH3 in EFFLUENT		0.577	0.102	0.420	0.140
MOLE % O2 in EFFLUENT		3.610	2.508	1.242	0.963
MOLES METHANOL OUT			0.025		0.010
MOLES MeOH FEED / MOLE NH3 IN BC EFFLUENT			2.47		1.89
PROPYLENE CONVERSION	mole %	98.042	97.109	99.021	98.866
METHANOL CONVERSION	mole %		90.912		92.967
					93.701
PRODUCT RESULTS and RESULTS :					
AN MAKE	gms/hr	54.343	54.198	51.056	50.795
HCN MAKE	gms/hr	5.820	8.699	9.831	11.364
RATIO HCN /AN	gms HCN/gm AN	0.107	0.161	0.183	0.224
NH3 Breakthrough	gms/hr	1.915	0.347	1.249	0.422
NH3 Reduction	gms/hr		1.568		0.827
					0.868

TABLE 1

		Example XIV		Example XV	
CATALYST:		3	3	1	1
REACTOR CONDITIONS :					
REACTOR TEMP	deg C	459	458	460	460
REACTOR PRESS	atms	2.02	2.02	2.02	2.02
METHANOL INJ POINT	cm's	41.91	41.91	41.91	41.91
WT % of CATALYST ABOVE the MeOH INJECTION PT.	%		26.52		12.88
CATALYST CHARGE	gms	578	578	375	375
REACTOR FEEDS :					
NH3 FEED	MOL/HR	1.882	1.861	1.425	1.426
C3H6 FEED	MOL/HR	1.299	1.299	1.299	1.299
AIR FEED	MOL/HR	13.772	14.122	14.249	14.25
N2 FEED (w/MeOH)	MOL/HR	0.374	0.374	0.374	0.374
METHANOL FEED	MOL/HR		0.251		0.139
NH3/C3H6 FEED	RATIO	1.203	1.202	1.097	1.096
AIR/C3H6 FEED	RATIO	10.503	10.573	10.970	10.971
MeOH/C3H6 FEED	RATIO		0.193		0.107
EFFLUENT CONDITIONS :					
MOLE % NH3 in EFFLUENT		0.400	0.000	0.412	0.091
MOLE % O2 in EFFLUENT		1.742	1.311	2.985	2.471
MOLES METHANOL OUT			0.033		0.012
MOLES MeOH FEED /MOLE NH3 IN BC EFFLUENT			3.50		1.85
PROPYLENE CONVERSION	mole %	99.022	97.927	99.182	98.766
METHANOL CONVERSION	mole %		86.828		91.675
PRODUCT RESULTS and RESULTS :					
AN MAKE	gms/hr	50.627	50.695	55.052	54.489
HCN MAKE	gms/hr	10.081	12.155	7.320	9.655
RATIO HCN/AN	gms HCN/gm AN	0.199	0.240	0.133	0.177
NH3 Breakthrough	gms/hr	1.222	0.000	1.278	0.286
NH3 Reduction	gms/hr		1.222		0.992

TABLE 1

Example XVI

CATALYST:

1	1
---	---

REACTOR CONDITIONS :

REACTOR TEMP	deg C	464	463
REACTOR PRESS	atms	2.02	2.02
METHANOL INJ POINT	cm's	41.91	41.91
WT % of CATALYST ABOVE the MeOH INJECTION PT.	%		12.88
CATALYST CHARGE	gms	375	375

REACTOR FEEDS :

NH3 FEED	MOL/HR	1.426	1.426
C3H8 FEED	MOL/HR	1.299	1.299
AIR FEED	MOL/HR	14.248	14.25
N2 FEED (w/MeOH)	MOL/HR	0.374	0.374
METHANOL FEED	MOL/HR		0.195
NH3/C3H8 FEED	RATIO	1.098	1.098
AIR/C3H8 FEED	RATIO	10.970	10.971
MeOH/C3H8 FEED	RATIO		0.150

EFFLUENT CONDITIONS :

MOLE % NH3 in EFFLUENT	0.403	0.009
MOLE % O2 in EFFLUENT	3.027	2.204
MOLES METHANOL OUT		0.026
MOLES MeOH FEED / MOLE NH3 IN BC EFFLUENT		2.65
PROPYLENE CONVERSION	mole %	99.196
METHANOL CONVERSION	mole %	86.517

PRODUCT RESULTS and RESULTS :

AN MAKE	gms/hr	54.223	54.047
HCN MAKE	gms/hr	7.187	9.471
RATIO HCN /AN	gms HCN/gms AN	0.133	0.175
NH3 Breakthrough	gms/hr	1.250	0.028
NH3 Reduction	gms/hr		1.222

TABLE 1

Example XVII

CATALYST:

1	1	1	1
---	---	---	---

REACTOR CONDITIONS :

REACTOR TEMP	deg C
REACTOR PRESS	atms
METHANOL INJ POINT	cm's
WT % of CATALYST ABOVE the MeOH INJECTION PT.	%
CATALYST CHARGE	gms

462	461	461	460
2.01	2.01	2.01	2.01
0.00	0.00	0.00	0.00

	100.00	100.00	100.00
400	400	400	400

REACTOR FEEDS :

NH3 FEED	MOL/HR
C3H8 FEED	MOL/HR
AIR FEED	MOL/HR
N2 FEED (w/MeOH)	MOL/HR
METHANOL FEED	MOL/HR
NH3/C3H8 FEED	RATIO
AIR/C3H8 FEED	RATIO
MeOH/C3H8 FEED	RATIO

1.426	1.652	1.702	1.717
1.299	1.299	1.299	1.299
14.25	16.509	16.76	16.766
0.374	0.374	0.374	0.374
	0.503	0.503	0.503
1.098	1.272	1.310	1.322
10.971	12.710	12.904	12.908
	0.387	0.387	0.387

EFFLUENT CONDITIONS :

MOLE % NH3 in EFFLUENT	
MOLE % CO2 in EFFLUENT	
MOLES METHANOL OUT	
MOLES MeOH FEED / MOLE NH3 IN BC EFFLUENT	
PROPYLENE CONVERSION	mole %
METHANOL CONVERSION	mole %

0.451	0.266	0.387	0.437
3.202	2.955	3.225	3.153
	0.006	0.006	0.006
	6.12	6.12	6.12
96.084	96.848	96.813	96.943
	98.900	98.889	98.888

PRODUCT RESULTS and RESULTS :

AN MAKE	gms/hr
HCN MAKE	gms/hr
RATIO HCN /AN	gms HCN/gm AN
NH3 Breakthrough	gms/hr
NH3 Reduction	gms/hr

55.639	54.078	54.826	54.585
8.943	15.262	15.825	15.829
0.125	0.282	0.286	0.286
1.398	0.978	1.444	1.632
	0.420	-0.045	-0.014

CLAIMS:

1. A process for making acrylonitrile by reacting propylene with ammonia and oxygen in a fluidized bed of ammonoxidation catalyst said process
5 being characterized by introducing vaporized methanol into the reactor under non-coking conditions at a point and in an amount selected such that the ammonia content of the reactor effluent is less than 0.5 mole percent and is lower than that obtained in a comparable process
10 in which no methanol is introduced and that the acrylonitrile production is at least 97 weight percent of that obtained in a comparable process in which no methanol is introduced, an inert gas being introduced with the methanol such that total linear gas flow
15 velocity through the orifices of the methanol introduction means exceeds the linear velocity of flow of other gases through the reactor.

2. The process of claim 1 wherein the linear velocity of gas flow through the orifices of the
20 methanol introduction means exceeds the linear velocity of flow of other gases through the reactor by ten to thirty times.

3. The process of claim 2 in which the ammonia content of the effluent is less than 0.25 mole
25 percent.

4. The process of claim 2 wherein acrylonitrile production is at least 99 weight percent of that obtained in a comparable process in which no methanol is introduced.

30 5. The process of claim 1 in which the methanol is mixed with at least 20 mole percent steam or air or mixture thereof.

6. The process of claim 5 in which the methanol is mixed with at least 20 mole percent steam.

- 20 -

7. The process of claim 6 wherein the amount of methanol introduced is controlled such that the methanol content of the effluent is less than 0.25 mole percent.

5 8. The process of claim 7 wherein the methanol content of the effluent is less than 0.01 mole percent.

10 9. The process of claim 5 wherein from 5 to 60 weight percent of the fluidized catalyst in the fluid bed reactor is above the methanol injection point.

15 10. The process of claim 1 wherein the orifices through which methanol is introduced are downwardly oriented and have least dimensions at least ten times larger than the mean particle size of the largest 10 percent by weight of the catalyst in the reactor.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/02206

A. CLASSIFICATION OF SUBJECT MATTER IPC 6 C07C253/26		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 6 C07C		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 638 546 (STANDARD OIL CO OHIO) 15 February 1995 see claims; examples ---	1-10
X	US,A,5 288 473 (SHAW WILFRID G ET AL) 22 February 1994 see claims; examples ---	1-10
A	US,A,3 911 089 (SHIRAISHI TATSUO ET AL) 7 October 1975 see column 4, line 36 - line 49 -----	1-10
<input type="checkbox"/> Further documents are listed in the continuation of box C.		<input checked="" type="checkbox"/> Patent family members are listed in annex.
* Special categories of cited documents : 'A' document defining the general state of the art which is not considered to be of particular relevance 'E' earlier document but published on or after the international filing date 'L' document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) 'O' document referring to an oral disclosure, use, exhibition or other means 'P' document published prior to the international filing date but later than the priority date claimed		
T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone Y' document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art & document member of the same patent family		
1 Date of the actual completion of the international search	Date of mailing of the international search report	
13 June 1996	25.06.96	
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl. Fax (+ 31-70) 340-3016	Authorized officer Pauwels, G	

INTERNATIONAL SEARCH REPORT

Int'l Application No

PCT/US 96/02206

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0638546	15-02-95	US-A-	5457223	10-10-95
		BG-A-	98453	31-05-95
		BR-A-	9400642	28-03-95
		CN-A-	1107464	30-08-95
		JP-A-	7053494	28-02-95
-----	-----	-----	-----	-----
US-A-5288473	22-02-94	BG-A-	98189	28-02-95
		US-A-	5457223	10-10-95
-----	-----	-----	-----	-----
US-A-3911089	07-10-75	JP-C-	1084669	25-02-82
		JP-A-	49095922	11-09-74
		JP-B-	55035377	12-09-80
		JP-C-	863922	13-06-77
		JP-A-	49058100	05-06-74
		JP-B-	51035400	01-10-76
		DE-A-	2350212	18-04-74
		DE-A-	2366002	30-06-77
		FR-A,B	2202034	03-05-74
		GB-A-	1426254	25-02-76
		NL-A-	8303480	01-02-84
		NL-A-	7313818	09-04-74
-----	-----	-----	-----	-----